DESIGN OF DIRECT METHANOL FUEL CELLS FOR PORTABLE APPLICATIONS

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Abstract

Direct Methanol Fuel Cells, due to the high energy content of methanol and simplicity of system design, present the possibility of achieving five to ten times the energy density of advanced lithium-ion rechargeable batteries. The design requirements, stack power density and efficiency issues for "mini" fuel cells (20-1000 W) and "micro" fuel cells (1-20 W) are discussed. Improvements in catalytic activity and reduced permeability of membranes to methanol are still significant to the reduction in the size and improving the overall efficiency of direct methanol fuel cell systems. Advances in alternate membranes and cost reduction strategies are discussed.

Introduction

The demand for power sources with high energy density has been steadily increasing. Advanced rechargeable lithium-ion batteries have made possible to realize as high as 150 Wh/kg. However, the need for frequent recharging and the requirement of electricity for recharging are the basic limitations of rechargeable batteries. Fuel cells operating on hydrogen and methanol are primary batteries that can be replenished with the active chemicals obviating the need for electrical recharging. Because of the inherently high energy content of hydrogen (32000 Wh/kg) and methanol(6000 Wh/kg), overall energy density values as high as 1500 Wh/kg can be conceived for fuel cell power sources even for a single charge of fuel; by replenishing of fuel operating times can be extended as long as needed. Thus fuel cells potentially address the fundamental limitations of battery power sources and have been actively considered for sometime now as a battery replacement.

Direct Methanol Fuel Cells

At the Jet Propulsion Laboratory, the focus has been on direct methanol fuel cells. In this type of fuel cell, an aqueous solution of methanol constitutes the fuel and is fed to a polymer electrolyte membrane based fuel cell. Briefly, with the direct methanol fuel cell system the complexity of processing the methanol into hydrogen is eliminated. The liquid feed operation also facilitates easy thermal management of the stack. Membrane electrode assemblies for methanol - air fuel cells are fabricated by bonding from catalyzed electrodes to either side of a proton conducting membrane in a manner similar to that used for hydrogen-air fuel cells. Platinum-ruthenium is the preferred catalyst for methanol oxidation and Pt for oxygen reduction. The important characteristics of this fuel cell have been discussed in earlier papers by the authors and other groups[1-7].

Over the last eight years, considerable advances have been made in increasing the power density of direct methanol fuel

cells. As a result power densities as high as 240 mW/cm^2 at 0.5 V have now been realized at 90° C operating on air at 20 psig. These advances have been key to designing systems that have significant power density and efficiency.

System Characteristics

Development of practically relevant integrated power direct methanol fuel cell systems is currently being pursued at the Jet Propulsion Laboratory [8]. Such portable systems have been classified as either "mini" fuel cells or "micro" fuel cells according to their power output range; power sources with output in the range of 1-20 W have now been conveniently classified as "micro" fuel cells and those with output in the range of 20-1000 W are called "mini" fuel cells. The distinction arises not only from the power range but also from the physical size and the type of stack and system architectures used. It is envisaged that applications such as battery replacement for cellular phones and laptops will use "micro" fuel cells while portable generators that could be used for communication, battery charging, remote power, emergency power, back-up power where size and mass constraints are not severe will use the "mini" fuel cells.

The schematic shown as Figure 1 is a diagram showing the elements and flow of substances in a typical direct methanol fuel cell system. This type of system architecture originated from the design of a 150-Watt system. In the current design for the 150-Watt system the power-producing element of the system namely, the stack, constitutes 45% of the weight system. In this design, the components are off-the-shelf and have not been specifically developed
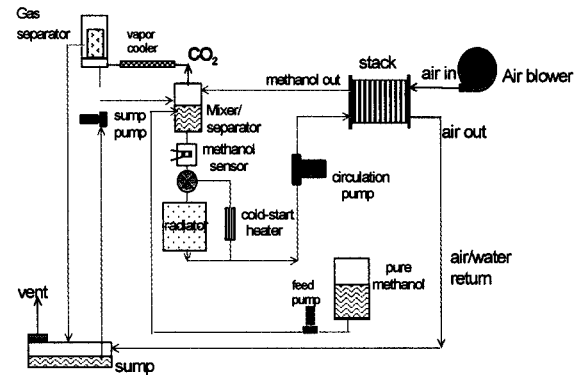

Figure 1. Schematic of a direct methanol fuel cell system

for this application. Hence there is substantial scope for further weight reduction. In the present design 15% of the stack power is used in supporting the balance of plant. The batteries are used for start-up and are internally recharged during fuel cell operation.

Power Density and Efficiency

At the current design point of 55-60°C the cell power density is about 70 mW/cm^2 at 0.40-0.45 V/cell. This result in power density values for the stack in
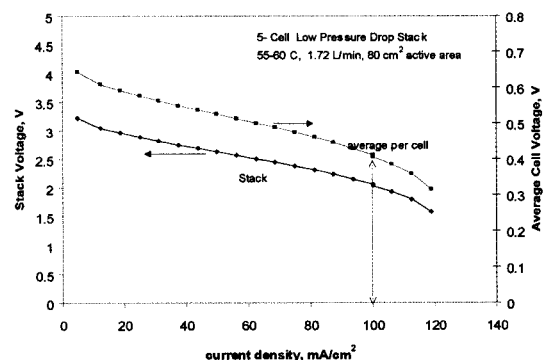
the range 75-100 W/kg at a stack efficiency of about 30%. Higher power densities have been realized at the cell level by operating at higher temperatures [3]. However, the continuous operation of a system such conditions is either impractical from maintaining a material and thermal balance and does not present a mass advantage at the system level [9].

The electrical performance of a five-cell 80 cm² stack using Nafion membranes operated under these design conditions is shown in Fig.2.

Figure 2. Performance of 5-cell diret methanol fuel cell stack under system operating conditions.

The stack power density of 75-100 W/kg is a consequence of the lower operating temperature, the need to operate close to ambient pressure, and, substantially reduced cathode performance due to methanol crossover. These are explained further. Since the electro-oxidation of methanol is a slow process compared to hydrogen oxidation, polarization losses to the extent of 0.35 V is associated with this process even on unsupported platinum-ruthenium catalysts. Thus development of more active catalysts for methanol oxidation will lead to higher power densities. Increasing the temperature of operation to enhance kinetics does increase the power density attainable with the cell. However, increase in temperature also raises the crossover rate[Tom's paper], water losses and in effect does not translate into improved system performance.

The parasitic power must be kept to a minimum in such small systems. This necessitates that the stack be operated close to the ambient pressure; the stacks must be designed such that the pressure drop to air flow is less than an inch of water. Under these conditions fans and blowers are preferred air moving devices. Such design requirements tend to increase the volume of the stack and manifolds. Further, the flow rate of air must not exceed 1.75 times the stoichiometric requirement in order that a water balance be maintained up to an

inlet air temperature of 42°C at 0% relative humidity [9]. Higher flow rates can be tolerated at lower inlet temperatures and higher values of relative humidity. Higher values of air flow rate can be used if water can be partially recovered. This would lead to increased stack power output. This is a design trade-off because water recovery involves increase in mass due to additional condensers and fans and also an increase in the power demand for ancillaries.

Operation at ambient pressure and low flow rates limits the partial pressures of oxygen in the air stream. Consequently, the cathode performance is impacted substantially by this design requirement. Membrane electrode assemblies with cathodes that can operate under these demanding conditions have been recently developed by the authors [10,11].

Further improvements to the cathode performance can be realized by reducing the methanol crossover to the cathode. Methanol crossing over to the cathode through the proton-conducting membrane is completely oxidized to carbon dioxide. However, this parasitic oxidation process increases the demand on oxygen from the air stream, reduces the number of catalytic sites and, enriches the interface with carbon dioxide that can further reduce the partial pressure of oxygen at the interface. As a result, the cathode is operating always under a mass transfer limited condition [6,10]. Thus the process of methanol crossover reduces the overall performance of the cathode. Thus the reduction of crossover is quite important to further reduction in the size of stacks for portable power systems.

Fuel Crossover

Membranes that reduce methanol crossover are key to realization of small and efficient portable systems. A membrane with low methanol permeability will allow operation at higher temperatures and higher methanol concentrations. Thus both efficiency and power density can be increased. To this end the University of Southern California in conjunction with JPL has been developing PSSA-PVDF membranes [11]. With these membranes the observed crossover fluxes are 25% of that observed with Nafion. These membranes also exhibit ionic conductivity comparable to Nafion and have demonstrated good chemical and thermal stability in short term experiments. Single cell studies have shown performance comparable to Nafion [11]. While this membrane has been evaluated for 60°C operation, the properties at higher temperatures need to be evaluated and understood. The work towards scale up of the laboratory process to prepare membranes reproducibly with the same properties is now being addressed. These are currently being implemented in a 80 cm^2 five-cell stack. Successful demonstration of these membranes will allow insertion of this technology into complete systems in the next year or so.

Regulating Methanol Concentration

Concentration of methanol in the fuel circulation loop (Fig. 1) has to be maintained at a set value to realize the desired efficiency and power density. Thus a methanol concentration sensor will always be an integral part of any type of direct methanol fuel cell power source design. An electrochemical methanol concentration sensor has been developed and tested at JPL [12]. This sensor can be used to monitor concentration levels ±0.01M in the range 0.1-3 M. This sensor was operated for several tens of hours and found to operate reliably as part of an automated feedback loop involving the feed of pure methanol.

Characteristics of Small Fuel Cells

As mentioned earlier, small fuel cells for cellular phone and laptop computers require to be configured differently in order to minimize mass and volume[13,14] These systems are most likely to operate close to the ambient temperature around the user considering that they will be handheld devices. Also, in some cases, natural convection could be the only method of air movement. The low temperature and the natural convection of air place additional limitations on the power density that can realized from direct methanol fuel cells. Flat-cell packs based on monopolar cells connected together and allow the attainment of higher voltages without the need for biplates. This type of design is particularly suited for low power density operation where the ohmic losses are minimal. Recent studies at JPL on intial prototype flat-cell pack with wick-feed of methanol have shown that power densities of about 10 mW/cm^2 can be realized. It is anticipated that with improved interconnect designs, a power densities of 20 mW/cm^2 can be achieved. Miniaturization of ancillaries still presents a significant design challenge. New designs for reactant/product handling, heat removal and power conversion that are highly efficient and maximize the use of the system resources needs to be developed. Fuel supply would be from ampoules or small cartridges. It is preferable that product disposal is also in cartridge form

and is arranged as part of the refueling process. In this manner, the user that is currrently accustomed to batteries, has minimal interaction with the water and carbon dioxide produced in the fuel cell. Operation at an ambient below $0^{\circ}C$, requires that the internal parts of the fuel cell are kept at slightly higher temperature so that start-up is not an issue. This is achieved by allowing the fuel cell to be "on" in a standby mode when exposed to such low temperatures.

Cost

It is important that fuel cell power sources are designed for manufacturing and has low material cost. JPL is currently developing d.c. magnetron sputter-deposition technique for applying catalytic layers on membranes and electrodes for fuel cell fabrication. Ultra-thin film catalyst layers so applied offer the prospect of reducing the catalyst requirement to about a tenth of current values[15], The process of magnetron sputtering is quite suited to mass-manufacturing. Also, alternate membranes based on PSSA-PVDF entail considerably lower material cost than Nafion . Molded graphite-polymer composite biplates will lead to considerable reduction in biplate fabrication costs.. Therefore, with the aforementioned improvements, a materials-alone cost estimate of about $200/kW seems to be quite achievable in the next three to five years.

Acknowledgement

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